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Fundamental studies of the adhesion of explosives to textile and non-textile surfaces

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Fundamental studies of the adhesion of explosives to textile and non-textile surfaces

Abstract

This paper describes the use of atomic force microscopy (AFM) to investigate the interactions between explosives crystals and different surfaces. Crystals of TNT, PETN and RDX were mounted onto tipless AFM cantilevers and repeatedly brought into contact with a range of surfaces (n=15), including textile and non-textile surfaces. The adhesion force during each contact was measured, and the results are presented in this work. The results suggest that explosives crystals display a higher adhesion to smoother, non-textile surfaces, particularly glass. This finding may be of use for forensic explosives investigators when deciding the best types of debris to target for explosives recovery.

Keywords

Explosives; detection; adhesion; analysis; forensic; explosions

Introduction

The recovery of explosives evidence from textile surfaces can be vital during a forensic investigation. When constructing an explosive device, it is likely that traces of explosives will be transferred to the bomb-maker's clothing [1, 2]. For example, traces of PETN were found on the clothing of the Oklahoma City bomber. Similarly, traces of explosives were found on the clothing of the foiled 'Millenium bomber' [2]. Other textile surfaces such as carpets have also been demonstrated to be a good matrix for retaining explosives, with nitrate ester explosives reported to have a particularly high affinity for such substrates [3]. As textile fabrics are ubiquitous and likely to be present at many post-blast scenes, they present good potential as sources for trace explosives evidence both at scenes or sites where explosive materials may have been constructed or transported.

Techniques for the recovery of explosives from non-porous surfaces typically involve the application of a cotton swab or polyester wipe, which may be either dry, or wetted with a solvent, to the surface of interest. Analysis is subsequently carried out on solvent extracts of the swab or wipe. A swipe sampling technique is also commonly used in airports, with a dry

swab (often made from glass fibre, Teflon or cotton, and coated with various polymers) wiped across passengers' hands, clothing and belongings [4].

Several techniques are in current use for the recovery of explosives traces from porous surfaces, although their recovery can be challenging [5]. Swabbing is also used to recover explosives residues from porous surfaces [1]. Compared to non-porous surfaces, solvent-swabbing is less successful. The use of solvents on fabrics may cause damage to the fabric in question. Additionally, when solvent-swabbing a piece of clothing, often only a general swab of the garment is taken, meaning that any sections containing high concentrations of explosives particles may be inadvertently passed over and not sampled [6]. Alternative methods for sampling porous surfaces include vacuum sampling [7, 8], solvent extraction [1, 9, 10] and direct sampling methods such as Raman spectroscopy and DESI-MS [5, 11-14]. However, these methods all have limitations. For example, vacuum sampling can only recover relatively large explosives crystals, solvent extraction may damage the surface of interest, and Raman spectroscopy requires an explosives crystal to be physically located on a surface before it can be analysed, which can be challenging due to the typically small size of explosives crystals. A recent promising candidate for sampling from textile surfaces is the contact heater [15], which heats a surface at the same time as drawing vacuum from it, with volatilised explosives captured within a sampling cartridge. This has proved successful for the recovery of TATP and EGDN from a variety of surfaces, including ceramic tiles, carpet and denim.

In order to improve the recovery of explosives from porous surfaces, a greater understanding is required of the fundamental interactions between explosives and these surfaces. Atomic force microscopy (AFM) provides an ideal means of assessing the interaction of explosives with different surfaces as it can measure the adhesive force between an explosives crystal and a surface of interest [4, 16]. This can be achieved by functionalising the end of a commercially-available tipless cantilever using an explosives crystal. The use of tipless cantilevers which have been functionalised in this manner is termed colloidal probe microscopy [16].

Zeiri *et al.* studied the adhesion of explosives crystals to various self-assembled monolayers. They mounted a self-assembled monolayer (SAM) or an explosives crystal onto the end of a tipless AFM cantilever, then measured the adhesion between the mounted SAM and an

explosive particle secured on a glass slide, or between the mounted explosive particle and a SAM secured on a glass slide. The monolayers contained a variety of end groups (-OH, -CH₃, -NH₂, -CF₃, -COOH, -C₆H₅, -C₃H₄SN), and they examined four explosives (TNT, RDX, HMX and PETN). The results of their study showed that the SAMs with -OH and -C₆H₅ end groups showed the strongest adhesion towards the explosives analysed [4].

Beaudoin *et al.* [16] used AFM to investigate the adhesion between TNT, RDX and PETN and three coated aluminium surfaces, bearing an acrylic melamine clear coat, a polyester acrylic melamine white coat or a green military-grade finish, of differing roughness. The authors found that the roughness of a substrate has a strong effect on the adhesion of an explosive crystal, with rougher surfaces tending to give lower adhesion than smoother surfaces. From this, it was concluded that the roughness of a surface has a much stronger contribution to any observed adhesion than the inherent chemical composition of such a surface [16].

Adya *et al.* used AFM to periodically analyse fibres exposed to different environmental conditions, to see how the surface texture changed over time [17]. They studied cotton, wool and viscose fibres exposed to various environmental conditions. However, although work has been independently performed using AFM to look at the adhesion of explosives to non-textile surfaces, or the morphology of textile fibres, to date no research has examined the adhesion of explosives crystals to a wider variety of surfaces, including textiles.

Although, as outlined here, a number of techniques are available with which to recover explosives residues from different surfaces, there is no fundamental research detailing the nature of the interaction of explosives with these different surfaces. This work enhances current knowledge and understanding through the determination of the fundamental, molecular-level interactions of three explosives (TNT, PETN and RDX) with a large variety of surfaces, including a number of textiles. Through this approach we provide an increased understanding of the interactions of explosive crystals with a range of different surfaces, facilitating a deeper understanding of the optimal target surfaces for sampling following an explosion. This knowledge may also enable the development of new methods with which to recover explosives from such surfaces.

Materials and methods

Fabrics

All fabrics analysed in this work were obtained from Spotlight Fabrics, Perth, Western Australia. The following fabrics were investigated in this work: rayon, silk, polyester stretch fabric, acetate, cotton jersey, wool, denim, calico natural cotton, mercerised cotton and polyester fleece.

Non-textiles

Aluminium foil was Confoil heavy duty catering foil brand; topography and adhesion measurements were performed on the matte side of the foil. A glass microscope slide (Biolab plain microscope slides, precleaned) was used for topography and adhesion measurements with glass. A Multix plastic lid was used as a source of polypropylene plastic for measurements. White and metallic orange car paint were obtained from car panels donated by Prestige Sunroofs WA sunroof fitters. The panels were close to factory finish.

AFM instruments

Topography and adhesion measurements were performed on a WITec alpha 300 SAR. A 20x (NA = 0.4) objective was used with this instrument. Data was collected using Control4 software. Cantilever functionalisation using explosives crystals was performed using a custom Nanoscope program using a Digital Instruments Dimension 3100 Atomic Force Microscope.

AFM analysis: Topographic measurements

Sample preparation

Textile fibre samples were prepared by laying a fibre across a piece of black double-sided adhesive tape (Stylus tapes brand) stuck to a clean glass microscope slide. The fibre was then taped at each end using a piece of adhesive tape, ensuring the fibres were not stretched during their preparation. Sample preparation for the non-textile surfaces was performed as follows: for the car paints, the paint surface was cleaned using ethanol then ultrapure water, then dried using a lint-free tissue. A small chip of paint was removed using a scalpel, and stuck down to a piece of black double-sided tape stuck to a glass microscope slide. Aluminium was treated in a similar manner: the matte surface was cleaned using ethanol and ultra-pure water, dried

using a lint-free tissue, then a small piece stuck down to a piece of double-sided tape on a glass microscope slide. For the adhesion to glass studies, a glass microscope slide was cleaned using ethanol then ultra-pure water, and dried with a lint-free tissue. A small piece of polypropylene plastic was cleaned using ethanol then ultra-pure water and dried with a lint-free tissue, before being placed directly on the sample stage for analysis, clipped in place by two microscope stage clips. A photomicrograph was taken of each surface prior to topographic measurements. This was performed using a 20x (NA = 0.4) objective and the WITec alpha300 SAR.

AFM probes used for topographic measurements

The topographies of all surfaces (with the exception of wool) were measured using WiTec AFM arrow cantilevers, reflex-coated, contact mode, nominal spring constant 0.2 N/m, 14 kHz. The topography of wool was obtained using a WiTec AFM arrow cantilever, reflex-coated, NC (AC) mode, spring constant 42 N/m, 285 kHz.

Topography measurements

All topographies were measured using contact mode AFM, with the exception of wool, which was measured in intermittent contact mode. For each textile fibre, the topography was measured at three separate regions along the length of the fibre. For the non-textile surfaces, the topography was measured at three distinct regions of the surface. An area measuring 16 x 10 μm was selected on each sample to be analysed. 256 points per line were used within this area, and 160 lines per image, to maintain a square pixel size. Time per line was 1 second. For the silk fibre, the topographies of three longer, narrower areas measuring 32 x 5 μm were measured, giving the same total scan area as for all other surfaces. 256 points per line, and 80 lines per image were used, to maintain a constant pixel size.

Surface roughness calculations

Surface roughness values of all 15 surfaces analysed were calculated using Project FOUR software, Version 4.0.14.11. All topography data were background corrected before extracting the root mean square roughness.

AFM analysis: Adhesion measurements

Chip preparation for adhesion measurements

Two sets of chips were used in this work. One set of explosives crystals was mounted onto the F cantilever of Bruker MLCT-O10 tipless silicon nitride cantilevers (spring constant 0.6 N/m). A second set of explosives crystals was mounted onto the A cantilever of Veeco NP-O cantilevers (spring constant 0.58 N/m).

Explosives crystal generation

The explosives used were supplied as standard solutions from Accustandard: TNT (1000 $\mu\text{g/mL}$ in MeOH:AcCN (1:1)); RDX (1000 $\mu\text{g/mL}$ in MeOH:AcCN (1:1)) and PETN (1000 $\mu\text{g/mL}$ in MeOH). A polytetrafluoroethylene (PTFE) sheet, 0.81mm / 0.031" thick, on which evaporation of explosives solutions was performed, was obtained from Alfa Aesar, MA, USA.

Explosives crystals were generated by evaporating standard solutions of the explosives, adapting the method employed by Beaudoin *et al.* [16]. For this, evaporation was performed on a piece of PTFE sheet (pre-cleaned using acetone and ultrapure water, then dried with a lint-free tissue). 20 μL of explosives solution was spiked onto the PTFE, and the solvent allowed to evaporate at ambient temperature. This took approximately one hour for PETN and RDX. In order to generate TNT crystals, a slightly different procedure was employed, again taking precedence from the work of Beaudoin *et al.* [16]. 20 μL of TNT solution (in 1:1 acetonitrile:methanol) was spiked onto a pre-cleaned and dried piece of PTFE and the solvent allowed to evaporate at ambient temperature. A white emulsion formed on the surface. To this emulsion, a 20 μL drop of ultra-pure water was added as a co-solvent. This facilitated the evaporation of the residual acetonitrile and methanol, removing the emulsion-like structure. Upon evaporation of the remaining water, TNT crystals were obtained. A minimum explosive crystal size of 10 μm was used for mounting onto the tipless cantilevers. This size takes precedence from the work of Beaudoin [16], who found that TNT crystals below this size were too fragile to work with. In each case it was ensured that the crystal diameter was below that of the explosive's respective critical diameters – the particle size above which shock or friction may cause the material to detonate. Literature values for these critical diameters are 2 mm for TNT [18], 0.5-1.5 mm for RDX [18, 19] and 1-1.5 mm for PETN [19].

Following generation of the crystals of explosives, their sizes were checked under an optical microscope. The size of each crystal was around 100 μm - too large to mount on a cantilever. The crystals were therefore milled between two clean glass slides, periodically checking the current crystal size under the optical microscope, until crystals of around 10 μm diameter

were obtained for each explosive. Images of the explosives crystals before and after milling are provided in Figure S-2.

Explosives crystal mounting onto tipless cantilevers

Explosives crystals were mounted onto tipless cantilevers using a Bruker Dimension 3100 Atomic Force Microscope instrument and Nanoscope software. A custom tip modification workspace was used for particle mounting. Optical microscope images of each explosive crystal at the end of a cantilever were taken prior to their use, and the cantilevers were checked periodically between adhesion measurements to ensure the explosive crystal was still present. An example of an RDX crystal mounted onto a cantilever and used during this work is shown in Figure 1.

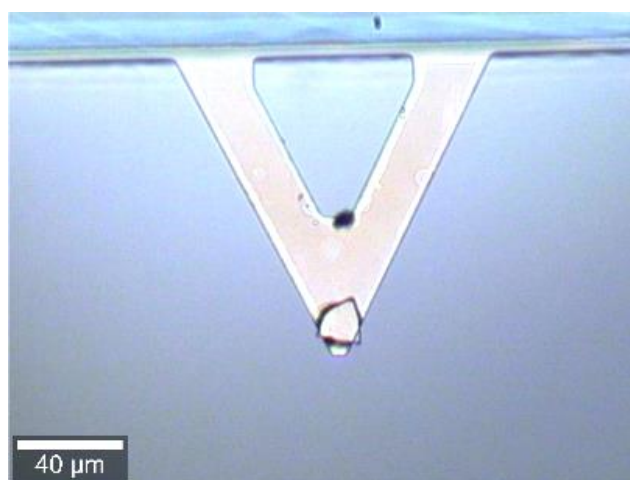


Figure 1. Photomicrograph of an RDX crystal mounted onto an AFM cantilever. Crystal size is approximately 14 μm.

Additional images of TNT- and PETN-functionalised cantilevers are provided in Figure S-3. Six explosives-functionalised cantilevers were prepared for this work: two each for TNT, PETN and RDX, with the adhesion measurements for a given explosive split between these two cantilevers.

Adhesion data collection

Adhesion measurements were performed using AFM Contact configuration, by taking individual force-distance curves across sixteen regions of each different surface. At each of the 16 regions, an average of 7 measurements was taken at the same position, with a total of 118 measurements obtained for each surface. The adhesion data collection process involved

repeatedly bringing the explosive particle mounted on the cantilever into contact with the surface of interest, before pulling the two apart and measuring the force required to separate the two. For each force-distance curve, 1000 data points were recorded. Each set of adhesion measurements was performed under ambient conditions. For the force curves, a small ‘push’ distance of 0.05 μm was used, to avoid damage to the explosives crystals. A pull of 2-3 μm was used in each case. A speed of 1 $\mu\text{m/s}$ was used.

Measurements were performed in a laboratory with controlled environmental conditions. Temperatures ranged from 16-24 $^{\circ}\text{C}$, and humidity levels were between 37 and 73 %.

Adhesion force data extraction

In order to compare the adhesion forces between different explosives and surfaces, the adhesion force values were extracted from the raw data generated from taking the force curves. For this, the raw data from the AFM (provided as a voltage value from the photodetector) was converted into a value representing the cantilever deflection (in nm) using a custom MatLab program. In conjunction with Hooke’s Law, this program then calculated the adhesion force present between the explosive and a given surface. This process is a standard AFM routine for force-distance curves. A copy of the MatLab program used is provided in the Supporting Information.

Results and discussion

Preliminary considerations

Explosives used for adhesion measurements

In this work, a variety of textiles were chosen for analysis, aiming to represent some of the most-commonly encountered textiles in forensic casework [10], as well as those examined by other researchers in the context of forensic explosives analysis [5, 12-14]. Although the main focus of this work was to investigate the adhesion of explosives to textiles, several non-textile surfaces were also investigated. These non-textile surfaces were chosen to represent surfaces which may be encountered at post-blast scenes, and included glass, aluminium, polypropylene plastic, metallic orange car paint and non-metallic white car paint.

Choice of explosives

Three explosives were used during this work: TNT, PETN and RDX. These represent three of the main classes of organic explosives which might be encountered during an investigation: nitroaromatics, nitrate esters and nitramines, respectively.

Adhesion measurements

It has been reported that the glue present for mounting particles has a negligible effect on a particle's surface properties [16]. This assertion holds true when the glue is restricted to the region between the explosive crystal and cantilever, to ensure that the glue does not interact with the surface under analysis, and when a very small droplet of glue is used, to ensure it is not absorbed by the explosive crystal which would otherwise affect its interactions. In the present work, the glue drops used were very small, and thus are not anticipated to have affected the measurements obtained. Due to their small size, the glue drops used are not visible in Figures 1 and S-3.

It should be noted that, due to the rough nature of the explosives crystal's surfaces, it is not possible to know the exact contact area between the particle and the surface being examined. Although this may appear to be problematic, it has been proposed [4] that this situation should, in fact, lead to the attainment of more realistic adhesion forces from the adhesion measurements. Larger adhesion forces are expected between a larger particle and a given surface, than a smaller particle and the same surface [16]. This is because a larger particle will have a higher mass, and more possible points of contact with the surface. For this reason, efforts were made during the present work to mount particles of as similar sizes as possible.

Surface photomicrographs and AFM topographies

Figure 2 contains selected photomicrographs (left column) and AFM 3D topographies (right column) of some of the textile and non-textile surfaces examined in this work, with images of the remaining surfaces displayed in the Supporting Information, Figure S-1.

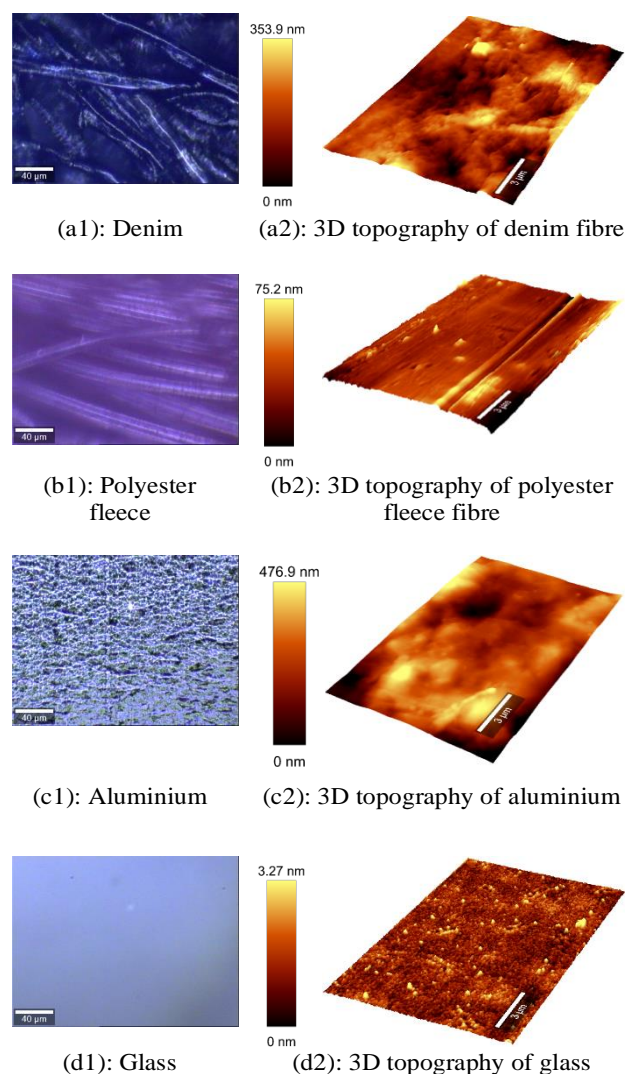


Figure 2. Selected optical photomicrographs and 3D AFM topographies of the surfaces analysed in this work

It can clearly be seen from Figure 2 and Figure S-1 that the various surfaces all display very different physical morphologies. A number of the textile surfaces (acetate, polyester fleece and rayon) display what appear to be ‘draw’ marks on their surfaces, likely originating from the extrusion process during formation of the textile fibres. Silk, as may be expected, displays a very smooth surface. For the silk fibre, an area twice as long and half as wide was mapped, compared to each of the other surfaces. This was because the silk fibre sample had a much narrower diameter than any of the other fibre samples, meaning it was not possible to measure the topography of areas measuring $16 \times 10 \mu\text{m}$, as the silk fibre’s diameter was around $10 \mu\text{m}$.

A number of the cotton-based surfaces (calico natural cotton, cotton jersey and denim) all show relatively uneven surfaces, and it can be seen that the wool surface also bears large ridges, likely from the scales present on the wool's surface. Wool has previously been shown [20] to be a good material for capturing traces of explosives, and one hypothesis for this may be that explosives particles can snag onto the surface of wool fibres, and be retained. In the present work, the topography of wool was measured in tapping mode, because the scales on the surface of the wool prevented the smooth measurement of a topography in contact mode (the cantilever tip was snagging on the boundaries between the scales).

The photomicrograph of aluminium (Figure 2 (c1)) displays many pits/ridges within the surface. These are also seen in the 3D topography (Figure 2 (c2)). In comparison to aluminium, glass displays a much smoother surface, with the elevation difference between the lowest and highest points on the glass 3D topography in Figure 2 (d2) only around 3 nm. Glass was the smoothest surface examined in this work. The photomicrograph of polypropylene reveals some small scratches present within the surface, which are reflected well in the 3D topography of the polypropylene (Figure S-1 (i2)).

Figure S-1 (j1) and (k1) show photomicrographs of the metallic orange and white car paint examined during this work, with their corresponding 3D topographies in Figure S-1 (j2) and (k2). These represent the topography of the uppermost clear coat layer of each paint. It is interesting to note that for each of the clear coats, visible 'pits' are present in the surface. There is therefore a possibility that these may be good receptacles for capturing particles of explosives at a post-blast scene.

Surface roughness

The SQ roughness of a surface can also be defined as the Root Mean Square roughness of the different heights recorded within the area, relative to a plane representing the mean of the measured height values running parallel to the sample plane. Figure 3 shows the average SQ roughness values obtained for each of the 15 surfaces. Each column represents the mean surface roughness from three separate topographic measurements on a given surface. The error bars show the standard deviation within these measurements.

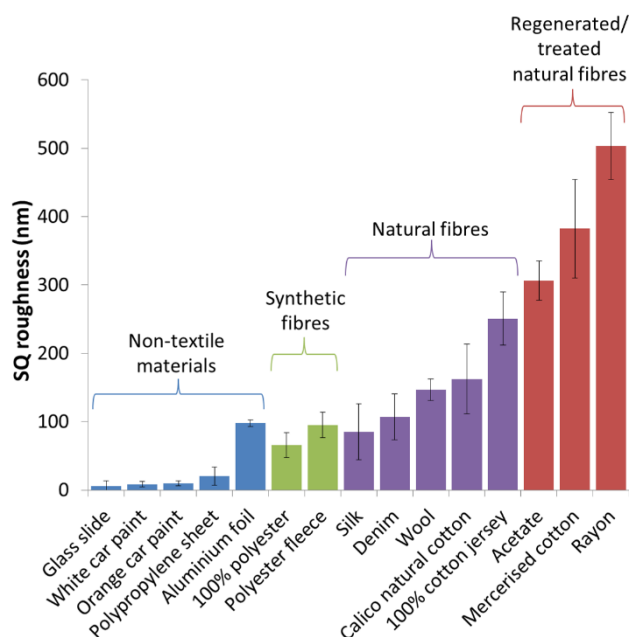


Figure 3. Average surface roughness values of the 15 surfaces investigated in this work, including non-textiles, synthetic fibres, natural fibres and regenerated natural fibres. Error bars show the standard deviation within a set of three measurements.

The surfaces have been classified into four different groups: non-textile materials, synthetic fibres, natural fibres and regenerated/treated natural fibres. Each group has been displayed in increasing order of roughness. Figure 3 clearly shows that the majority of the non-textile materials (with the exception of aluminium) are smoother than any of the textile surfaces examined. This was also evident from the topographic images displayed in Figure 2 and Figure S-1. Aluminium foil demonstrates the highest surface roughness from the non-textile materials; its roughness is comparable to that of the synthetic fibres. Generally, the natural fibres are rougher than the synthetic fibres, and the regenerated/treated natural fibres are rougher still. This is as expected, as the additional processing steps involved in the regeneration or treating of fibres is likely to cause some additional physical roughness.

The adhesion of explosives to 15 different surfaces

Beaudoin *et al.* [16] used AFM to measure the adhesion between three explosives and three painted aluminium surfaces of different roughnesses, finding that the explosives had a higher adhesion to smoother surfaces. The authors hypothesised that the major source for this difference was due to the different physical roughnesses of the surfaces [16]. It was therefore considered that their finding may apply to the adhesion measurements of this work.

Considering Beaudoin's finding, it should be expected that a higher adhesion should be recorded between the explosives used in this study and the smoothest surfaces illustrated in Figure 3 – the non-textile surfaces. In contrast, the lowest adhesion would therefore be expected between the explosives and the regenerated/treated natural fibres, owing to their high surface roughness.

Beaudoin's work only considers physical roughness when correlating adhesion to surfaces. Zeiri *et al.* [4] instead focused on the chemical characteristics of a surface with regards to the adhesion of explosives. They functionalised cantilevers with explosives and then measured the adhesion forces between 4 explosives and various self-assembled monolayers with different end-groups. They found the highest adhesion between explosives and the self-assembled monolayers which had hydroxyl and phenyl end groups.

Although Beaudoin and Zeiri's findings are interesting, each study only considered one parameter with respect to the adhesion of explosives – physical roughness or chemical composition. The current study therefore aimed to investigate the contribution of both physical roughness and chemical composition, to assess the significance of these parameters when considering the adhesion of explosives to a given surface. Several of the surfaces examined in this study have, for example, hydroxyl groups at the surface (glass, denim, cotton jersey, natural cotton, rayon), yet they each have very different physical roughnesses, as illustrated in Figure 3.

If adhesion is most-strongly dependent on the chemical composition of a surface, similar adhesion may be expected to each of those surfaces. On the other hand, if adhesion is more highly-dependent on a surface's physical roughness, higher adhesion should be seen to glass, and a much lower adhesion should be seen to rayon, as this is a much rougher surface. It should be noted that, for the textile surfaces, the adhesion was measured between the mounted explosives crystals and single fibres extricated from each of the textile surfaces, rather than using a larger swatch of each textile. This current work is designed to act as a 'starting point' to provide an initial method which can then be further developed using larger scale systems. For this reason, in the current work, adhesion was measured to individual textile fibres. In addition, although it may be envisaged that, with a larger piece of fabric bearing a 'mesh' type structure, explosives crystals may have the potential to become embedded in the gaps of the mesh, this scenario would involve *physical* adhesion, which

would be the case for any type of particle, rather than just explosives. The present work is therefore more concerned with the *chemical* adhesion between explosives and a textile fibre surface.

Figure 4 contains the adhesion data obtained between TNT, PETN and RDX across the 15 different surfaces studied. Individual adhesion graphs for each of the three explosives are also displayed in Figures S-4 to S-6. Each column represents the mean of 118 adhesion measurements between a given explosive crystal and a given surface. The error bars indicate the standard deviation within the set of measurements.

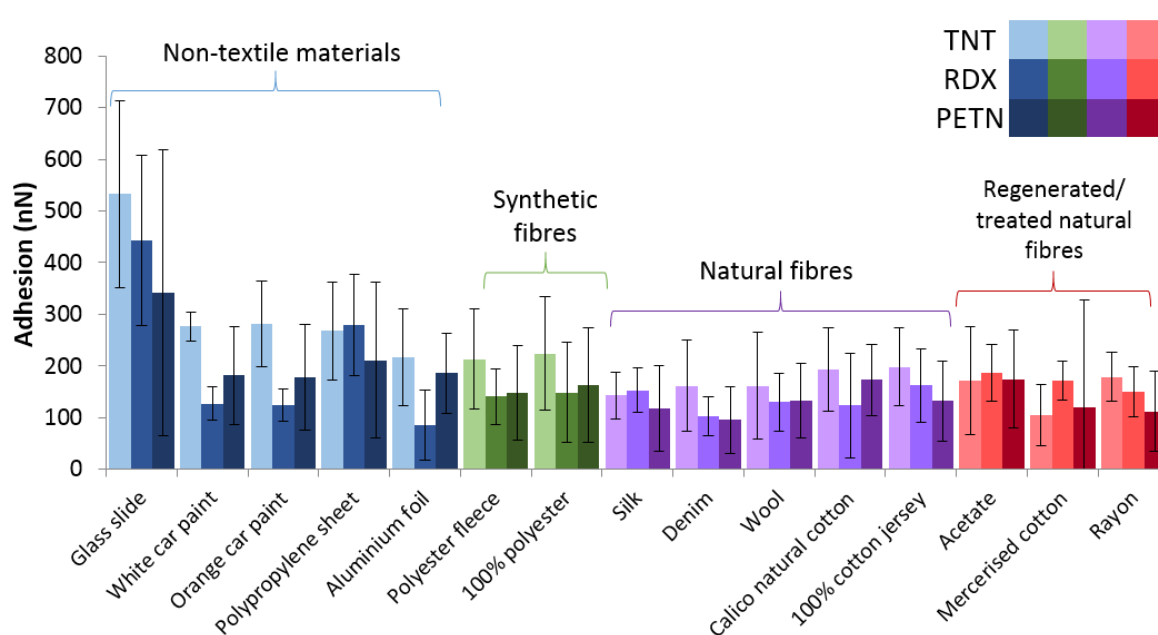


Figure 4. Graph showing average adhesion measurements between TNT, PETN and RDX with 15 different surfaces. Error bars show standard deviations within the 118 adhesion measurements for each surface

Although it may appear that the standard deviations for a given set of measurements are quite high, this effect is not thought to be due to any inherent problems resulting from the nature of the data collection. Instead, these standard deviation values are attributed to the irregular surface morphology of the mounted explosives crystals, and possible variations in surface morphology across a given surface [4, 21].

In the optical microscope images of cantilevers functionalised with TNT, PETN and RDX crystals (Figure 1 and Figure S-3), it can be seen that the morphologies of the crystals are

very rough. These rough surfaces may lead to multiple points of contact with a given textile fibre. It is also possible that regions of differing morphology in the crystals may give rise to varying areas of contact between the explosive and a given surface [4].

As well as depending on the crystal's surface structure, the number of points of contact also depend on the morphology of the surface at any given point, and the degree of complementarity between the crystal and a surface at a given measurement point. For example, Beaudoin *et al.* suggest that with a smoother surface, the level of interpenetration between an explosive crystal and a surface is likely to be higher than that for a rough surface. Due to the unknown nature of a rough surface, the peaks and valleys on an explosive crystal and the surface it is placed in contact with may have only a low degree of complementarity [16], resulting in fewer points of contact between the explosive crystal and the surface. For this reason, rather than attempting to normalise the data obtained in this work, attempts were made to use explosives crystals of approximately the same diameter for a given set of surfaces (ranging from 14 to 20 μm ; see Figures 1 and S-3), and to take force-distance curves across a large number of different points on a given surface, to generate representative data for a given combination of explosive and surface. It is acknowledged that the error bars displayed in Figure 4 are large.

Taking each explosive in turn, trends can be observed. For TNT, a particularly high adhesion can be observed to the glass slide, which was the smoothest surface examined in this work. Accounting for the error bars on Figure 4, TNT displays very little difference in its adhesion to the different surfaces, with the exception of the glass slide. However, despite these error bars, some potential trends may be seen to be emerging, with a tendency of the TNT to display a higher adhesion to the smoother, non-textile surfaces. TNT demonstrates a lower adhesion to aluminium foil than to any of the other non-textile materials. Aluminium foil had the highest roughness of all of the non-textile materials (see Figure 3), so this was expected, based on the conclusions from Beaudoin's work [16].

The aluminium foil used in this work is formed from only a single chemical element. This therefore limits the potential types of interactions possible with an explosive crystal, compared to, for example, wool, which is formed from a wide variety of amino acids and hence will have a number of different functional groups on its surface with which to interact with an explosives crystal. This factor alone seems to suggest that chemical composition

plays a lesser role than other properties such as surface roughness. On the other hand, compared to the smoothest non-textile surfaces (glass, car paint and polypropylene), TNT displayed a much lower adhesion to the textile surfaces.

With regards to PETN, a higher degree of variation can be seen within the recorded average adhesions compared to the adhesion between TNT and the 15 surfaces. A very high adhesion force appears to form between PETN and glass, whereas a much lower adhesion force is present between PETN and the white and orange car paint. This is interesting, as the two both have similar surface roughnesses (see Figure 3), suggesting that in this case, the chemical nature of the surface may play a role, with the chemical composition of glass interacting more favourably with PETN than the chemical composition of the white car paint and orange car paint clear coats. This suggests that car paint clear coat is a poorer surface for capturing PETN compared to glass.

It can be seen that PETN displays a particularly high adhesion to glass and polypropylene, with a lower adhesion to the remaining surfaces. One point to note is that in this work, the adhesion force between a bare PETN crystal was examined with the 15 different surfaces, rather than a polymer-coated PETN crystal as might be found in a plastic explosive. This is also the case for the work of Zeiri and Beaudoin [4, 16]. The PETN examined in this work is therefore representative of the free-flowing PETN crystals found in detonating cord and some explosives boosters, rather than the polyisobutylene or styrene butadiene polymer-coated crystals found in many plastic explosives [22]. It would be of benefit in future work to also investigate coated explosives crystals originating from plastic explosives as these results would be of use with regards to pre-blast explosives detection.

Finally, RDX, like TNT and PETN, demonstrates a very high adhesion to glass. This result seems to suggest that glass is a good substrate for capturing RDX residues. It is known that glass fibre swabs are in use for some airport-based sampling, so this approach would appear to be very suitable for the recovery of RDX, TNT and PETN [4]. The adhesion measured between RDX and the white and metallic orange car paints is similar; lower than that to glass. With regards to the adhesion of RDX to the 10 different textile materials examined, it can be seen that the adhesion of RDX to the textile materials appears to follow a similar trend to TNT and PETN with the different textiles.

Overall, it can clearly be seen from Figure 4 that all of the explosives crystals have a tendency to have a higher adhesion to the non-textile surfaces than to any of the textile surfaces. Combining the data from both Figure 3 and Figure 4, a broad conclusion can be made that the explosives demonstrate higher adhesion to smoother surfaces. This finding is in excellent agreement with the findings of Beaudoin *et al.* [16], who found a higher adhesion between explosives and smoother painted aluminium surfaces.

It should be noted that Beaudoin's work only examined adhesion due to the presence of van der Waal's forces [16]. However, it is likely that textiles may have traces of water absorbed onto their surfaces. Adya [17] reports high water absorption onto viscose and rayon fibres due to the presence of hydroxyl groups on the fibre surfaces. Similarly, Zeiri *et al.* [4] found that explosives had the highest adhesion to hydroxyl and amine end groups and suggested that this may be due to adsorption of water molecules onto these end-groups, which could then form a water bridge to the explosives crystals. They proposed that such capillary forces may be the dominant factor contributing towards the adhesion force between an explosives crystal and a given surface. Although effects due to humidity may have influenced our recorded adhesion measurements, humidity is also likely in real-life situations so we believe that this is acceptable.

In particular, it can be seen from Figure 4 that each of the three explosives displayed the highest adhesion to glass, the smoothest surface examined in this work and with a surface primarily composed of hydroxyl groups. This finding is therefore in strong agreement with both the findings of Beaudoin [16], who found the highest adhesion between explosives and smoother surfaces, and Zeiri [4], who showed explosives have a strong adhesion towards hydroxyl groups. Comparatively lower adhesion values were obtained between the explosives and the cellulose-based textiles (denim, calico natural cotton, mercerised cotton and rayon), which would also bear surface hydroxyl groups. This finding suggests that the adhesion of explosives to a surface is more strongly-dependent on how rough or smooth a surface is, rather than the chemical nature of the surface itself.

Conclusions

This research has investigated the adhesion of explosives to a variety of textile and non-textile surfaces using AFM. Although previous AFM studies have investigated the adhesion of explosives to vehicle paints and monolayers, no previous work has been performed to investigate the adhesion of explosives to the wide variety of textiles and non-textiles explored in this work. These findings thus fill that gap, providing vital, fundamental knowledge regarding the interactions of explosives crystals with a variety of surfaces.

Surface roughness measurements demonstrated that non-textile surfaces tend to be much smoother than any textile surfaces. Following this, 118 adhesion measurements were obtained between TNT, PETN and RDX and each of the 15 different surfaces, to give a total of over 5,000 measurements. The results suggest that the explosives have a higher adhesion to smoother surfaces (in this case, the non-textile surfaces), with a particularly high adhesion observed between the three explosives and glass (the smoothest surface examined). This result is in strong agreement with previous literature [4, 16] which found the highest adhesion of these explosives to smoother surfaces, and surfaces bearing surface hydroxyl groups, respectively.

Based on the results of this work, it may be prudent to sample smooth pieces of debris, such as glass, following an explosion, to attempt to maximise the quantity of recovered explosives. In addition, the results of this work are also of potential benefit towards enhancing the detection of pre-blast explosives residues (such as for aviation security). A key consideration with this work is that even if an explosive does display a high adhesion to a surface, this is no guarantee that it will also demonstrate a high persistence to this surface, or, on the other hand, a high adhesion may make it difficult to recover explosives traces from a given surface, so these possibilities will be investigated in future work to give a broader understanding of the nature of the interaction of explosives with a variety of surfaces.

In the present work, explosives crystals were generated by evaporating solutions of explosives, and we acknowledge that the shape of these crystals may differ from those manufactured for industrial use. This is because this work aimed to use a very simple model system to develop a method of analysis. This method may then be used in the future for more complex systems, such as those involving industrial grade explosives crystals. It would be

interesting in a piece of future work to compare the adhesion between explosives crystals generated by evaporation of standard solutions, and explosives crystals generated by bulk industrial manufacturing. In addition, this work has primarily focused on the interaction of explosives with new, clean surfaces. However, it would be forensically useful to also consider some non-ideal cases, which may be more representative of a real-life scenario. One such example would be investigating the adhesion of explosives to laundered fabrics, likely containing traces of washing powder [23] which may affect the adhesion of explosives to the fabric. Similarly, wearing or washing fabrics may also cause a change in the properties of a surface [23]. Work by Adya *et al.* [17] has shown that fibres become rougher upon exposure to environmental conditions. Based on the conclusions from this work, this would suggest that a roughening of the fibres would give rise to a lower adhesion from explosives. This hypothesis would therefore be interesting to investigate in the future.

References

- [1] I. Corbin, B. McCord, Detection of the improvised explosives ammonium nitrate (AN) and urea nitrate (UN) using non-aqueous solvents with electrospray ionization and MS/MS detection, *Talanta*, 115 (2013) 533-539.
- [2] Forensic chemistry handbook / edited by Lawrence Kobilinsky, Hoboken, N.J. : John Wiley & Sons, Hoboken, N.J., 2012.
- [3] R.A. Strobel, Recovery of material from the scene of an explosion and its subsequent forensic laboratory examination - a team approach, in: A. Beveridge (Ed.) *Forensic Investigation of Explosions*, Taylor & Francis, London, 1998, pp. 101-131.
- [4] Y. Zakon, N.G. Lemcoff, A. Marmur, Y. Zeiri, Adhesion of Standard Explosive Particles to Model Surfaces, *J. Phys. Chem. C*, 116 (2012) 22815-22822.
- [5] N. Talaty, C.C. Mulligan, D.R. Justes, A.U. Jackson, R.J. Noll, R.G. Cooks, Fabric analysis by ambient mass spectrometry for explosives and drugs, *Analyst*, 133 (2008) 1532-1540.
- [6] G.T. Murray, The significance of analytical results in explosives investigation, in: A. Beveridge (Ed.) *Forensic Investigation of Explosions* (2nd edition), CRC Press, Boca Raton, FL, 2012, pp. 725-739.
- [7] *Encyclopedia of forensic sciences* / edited by Jay Siegel, Pekka Saukko, Oxford : Elsevier, Oxford, 2013.
- [8] S. Doyle, Quality and the trace detection and identification of organic high explosives, in: A. Beveridge (Ed.) *Forensic Investigation of Explosions* (2nd edition), CRC Press, Boca Raton, FL, 2012, pp. 539-583.
- [9] V. Cavett, E.M. Waninger, J.J. Krutak, B.A. Eckenrode, Visualization and LC/MS analysis of colorless pepper sprays, *J. Forensic Sci.*, 49 (2004) 469-476.
- [10] H. Brust, A. van Asten, M. Koeberg, A. van der Heijden, C.-J. Kuijpers, P. Schoenmakers, Pentaerythritol tetranitrate (PETN) profiling in post-explosion residues to constitute evidence of crime-scene presence, *Forensic Sci. Int.*, 230 (2013) 37-45.

- [11] E.M.A. Ali, H.G.M. Edwards, I.J. Scowen, Raman spectroscopy and security applications: the detection of explosives and precursors on clothing, *J. Raman Spectrosc.*, 40 (2009) 2009-2014.
- [12] E.M.A. Ali, H.G.M. Edwards, I.J. Scowen, In-situ detection of single particles of explosive on clothing with confocal Raman microscopy, *Talanta*, 78 (2009) 1201-1203.
- [13] C. Hubert, X. Machuron-Mandard, J.-C. Tabet, Ambient ionization MS analysis of swabs used for explosives detection, *LC-GC Eur.*, (2013) 8, 10-13.
- [14] S. Almaviva, S. Botti, A. Palucci, A. Puiu, F. Schnurer, W. Schweikert, F.S. Romolo, Application of micro-Raman spectroscopy for fight against terrorism and smuggling, *Opt. Eng.* (Bellingham, WA, U. S.), 53 (2014) 044113/044111-044113/044117.
- [15] H.A. Yu, S.W. Lewis, M.S. Beardah, N. NicDaeid, Assessing a novel contact heater as a new method of recovering explosives traces from porous surfaces, *Talanta*, 148 (2016) 721-728.
- [16] M.N. Chaffee-Cipich, B.D. Sturtevant, S.P. Beaudoin, Adhesion of Explosives, *Anal. Chem.* (Washington, DC, U. S.), 85 (2013) 5358-5366.
- [17] E. Canetta, K. Montiel, A.K. Adya, Morphological changes in textile fibers exposed to environmental stresses: Atomic force microscopic examination, *Forensic Sci. Int.*, 191 (2009) 6-14.
- [18] J.W. Grate, R.G. Ewing, D.A. Atkinson, Vapor-generation methods for explosives-detection research, *TrAC, Trends Anal. Chem.*, 41 (2012) 1-14.
- [19] N. Kubota, *Combustion of Explosives, Propellants and Explosives*, Wiley-VCH Verlag GmbH & Co. KGaA2007, pp. 257-272.
- [20] A. Beveridge, Editor, *Forensic Investigation of Explosions*, Taylor & Francis1998.
- [21] T. Das, T. Becker, B.N. Nair, Measurements on hydrophobic and hydrophilic surfaces using a porous gamma alumina nanoparticle aggregate mounted on Atomic Force Microscopy cantilevers, *Thin Solid Films*, 518 (2010) 2769-2774.
- [22] J.M. Connelly, W.C. Curby, F.T. Fox, S.F. Hallowell, Detection of hidden explosives, in: A. Beveridge (Ed.) *Forensic Investigation of Explosions*, Taylor & Francis, London, 1998, pp. 45-73.
- [23] *Interpretation of Fibres Evidence, Forensic Examination of Fibres*, Second Edition, CRC Press1999.